Correlation of the Magnetically Induced Directional Order with the AB_3-Type Superlattice

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Synopsis

The directional order induced by magnetic anneal in the ferromagnetic face-centered cubic binary solid solution and its correlation with the ordinary superlattice of the AB_3 type are calculated by the quasi-chemical method using quadruplets approximation. The anisotropic long-range order parameters and sixty four parameters representing the numbers of different quadruplets are introduced to describe both the directional and ordinary order, and their equilibrium values in the magnetically annealed state are calculated. It is shown how the formation of short-range and long-range orders during magnetic anneal depresses the occurrence of the directional order and thus of the additional uniaxial ferromagnetic anisotropy. The change caused by ordering in the directional property of the induced ferromagnetic anisotropy is indicated. The results obtained can explain the observed irregular behavior of the induced ferromagnetic anisotropy in the magnetically annealed Ni_3Fe single crystal.

I. Introduction

It is well known that, when a crystal of ferromagnetic solid solution is annealed in an applied magnetic field, a certain crystallographic direction near the direction of the applied field becomes an easy direction of magnetization, and thus a uniaxial magnetic anisotropy is additionally induced in the crystal.[1] Since this magnetic anneal effect may give a drastic change in the magnetic behavior of a ferromagnetic solid solution alloy, it has been studied experimentally and theoretically by many investigators.

The mechanism now accepted as the most probable origin of this effect is as follows: During the magnetic anneal, the so-called directional order, i.e., the anisotropic distribution of nearest-neighbor atom pairs is induced so as to reduce the free energy (including the magnetic anisotropy energy) of the system, the induced uniaxial magnetic anisotropy being originated from this directional order [2]~[7]. Although the theory[3]~[5] developed on the basis of this mechanism can

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(1) See, e.g., R.M. Bozorth: Rev. Mod. Phys., **25** (1953), 42; S. Kaya: Rev. Mod. Phys., **25** (1953), 49.
(2) S. Chikazumi: J. Phys. Soc. Japan, **5** (1950), 327 and 333.
(3) L. Néel: J. de phys. rad., **15** (1954), 225.
(4) S. Taniguchi and M. Yamamoto: Sci. Rep. RITU, **A 6** (1954), 330.
(5) S. Taniguchi: Sci. Rep. RITU, **A7** (1955), 269.
(6) S. Chikazumi and T. Oomura: J. Phys. Soc. Japan, **10** (1955), 842.
(7) S. Chikazumi: J. Phys. Soc. Japan, **11** (1956), 551.

describe the general aspects of the induced magnetic anisotropy, there remain some inconsistencies between the theory and the experimental facts. The theory predicts that the uniaxial magnetic anisotropy induced in binary ideal solid solutions depends upon the concentration of solute atoms, q, as $q^2(1-q)^2$, but actually the magnetic anisotropy induced in Ni-Fe alloys,[6),(8)] and in Ni-Co alloys[9)] shows considerable deviations from such a simple concentration dependence. It has also been found that the dependence of the magnetic anisotropy induced in Fe-Co alloys on the concentration[10)] and the annealing temperature[11)] shows an anomalous behavior due to the superlattice formation. Further, the experiments [7),(12),(13)] indicate, in accordance with the theory, that the orientational dependence of the induced magnetic anisotropy energy in a single crystal specimen is expressed by

$$K = -k_1 \sum_i \beta_i^2 \beta_i'^2 - k_2 \sum_{i>j} \beta_i \beta_j \beta_i' \beta_j' \ , \qquad (1)$$

where β_i and β_i' $(i=1, 2, 3)$ are the direction cosines of the annealing magnetic field and of the measuring magnetic field, respectively. But, according to the experiments,[7),(12),(13)] the ratio of the factors, k_2/k_1, varies with the concentration and with the condition of heat treatment, although the theory requires that k_1 is equal to zero for the body-centered cubic lattice and k_2/k_1 takes a fixed value of 4 for the face-centered cubic one.

In view of these circumstances, it is required for the theory that the effect of non-ideality of solid solutions has to be taken into consideration. In fact, Néel[3)] has treated the case of non-ideal solutions, but this treatment cannot evaluate strictly the correlation of the directional order with the non-ideality of solid solutions, since it does not take into account the mixing entropy of the atomic configuration including the directional order. It is hardly needless to say that it also does not yield an explicit expression for the effect of long-range order.

Thus, it may be of value to formulate the statistical thermodynamics of non-ideal solutions including the directional order and to examine the relation of the directional order with the short-range and long-range orders or with clustering. Such a theoretical consideration will lead to a clear understanding of the formation process of the directional order in real substances and, at the same time, it will give some information about the supperlattice formation or clustering. Along this line, the present author reported[14)] a statistico-thermodynamical treatment of body-centered cubic non-ideal solid solutions involving the directional order. In that paper, anisotropic short-range order parameters and a long-range

(8) E.T. Ferguson: Compt. rend., **244** (1957), 2363.
(9) M. Yamamoto, S. Taniguchi and K. Aoyagi: Sci. Rep. RITU, **A13** (1961), 117.
(10) J. Maréchal: J. de phys. rad., **16** (1955), 122S.
(11) E.T. Ferguson: J. de phys. rad., **20** (1959), 251.
(12) K. Aoyagi, S. Taniguchi and M. Yamamoto: J. Phys. Soc. Japan, **13** (1958), 532.
(13) K. Aoyagi: Sci. Rep. RITU, **A13** (1961), 137.
(14) T. Iwata: Sci. Rep. RITU, **A10** (1958), 34.

order parameter were introduced, in terms of which the free energy of ferromagnetic solid solutions could be formulated. By minimizing the free energy, the equilibrium values of these parameters were obtained, and thus the behavior of the directional order was expressed as a function of the concentration and the magnetic annealing temperature. The results obtained could explain the experimental observations of an anomalous behavior of the uniaxial ferromagnetic anisotropy induced in magnetically annealed Fe-Co alloys.

In the present study a similar treatment is applied to the face-centered cubic binary non-ideal solid solution, and the behavior of the directional order coexisting with the superlattice of the AB_3 type is examined. In this case, the quadruplets approximation[15] has to be employed in order to avoid a complication involved in the close-packed lattice. Moreover, both of the short-range and the long-range atomic configuration become anisotropic. Then three anisotropic long-range order parameters and sixty four parameters representing the numbers of different quadruplets are introduced.

II. Notations and geometrical relations

Let us consider a face-centered cubic alloy of the type AB_3, the total number of atoms being N. A face-centered cubic lattice may be divided into four sublattices, I, II, III, and IV, as shown in Fig. 1. In general, they may not be equivalent to each other, since we are now interested in both the directional order and the AB_3-type superlattice. Anisotropic long-range order parameters, r_i ($i=1, 2, 3, 4$), are defined so that the probability that a lattice point belonging to the I, II, III, or

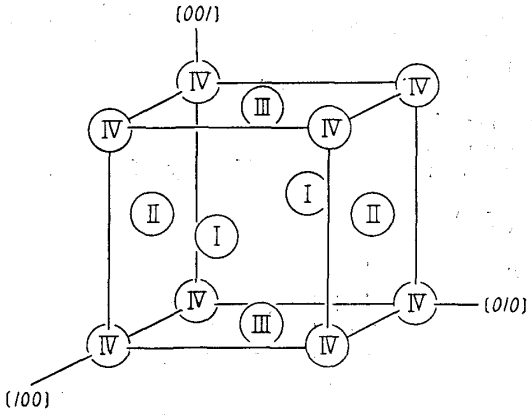


Fig. 1. Four sublattices in the face-centered cubic lattice.

IV sublattice is occupied by an A atom may be $(1-r_1)/3$, $(1-r_2)/3$, $(1-r_3)/3$, or r_4, respectively.

Next, we consider a system of N tetrahedral quadruplets constructed by four neighboring lattice sites, each of which belongs to one of the four sublattices (Fig. 2), in such a way as the total number of pairs of neighboring lattice sites may have

(15) See E.A. Guggenheim: *Mixtures*, Oxford U.P., Oxford (1952), p. 136.

the correct value of $6N$ for a crystal consisting of N lattice sites. Six edges of each quadruplet are along the [011], [0$\bar{1}$1], [101], [$\bar{1}$01], [110], and [1$\bar{1}$0] nearest neighbor directions, which are labeled as 1, 2,..., and 6, respectively, as shown in Fig. 2. These quadruplets may be divided into four groups with respect to their aspect, which are labeled as i, ii, iii, or iv according as the center of the quadruplet lies in the [111], [$\bar{1}\bar{1}$1], [1$\bar{1}\bar{1}$], or [$\bar{1}$1$\bar{1}$] direction passing through their corner site belonging to the sublattice IV as shown in Fig. 2. There are sixteen manners of atomic occupation for each group of the qudruplets, since each of the four corners

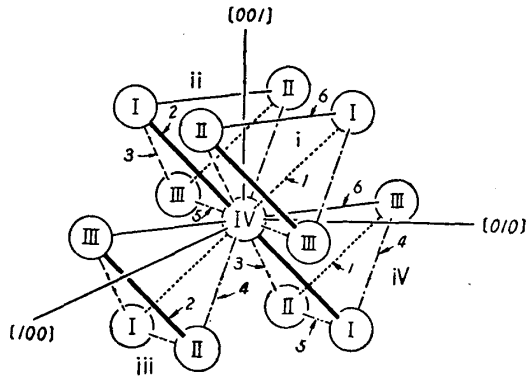


Fig. 2. Directions of the edges (indicated by Arabic numerals) and four aspects (indicated by small Roman numerals) of tetrahedral quadruplets.

Table 1. The sixteen manners of atomic occupation of the jth group ($j = 1, 2, 3, 4$) of tetrahedral quadruplets in a face-centered cubic lattice, numbers of the quadruplets so occupied, and their energies.

No.	Manner of occupation	Number of quadruplets so occupied	Energy of the quadruplet
	I II III IV	$\times(N/4)$	
1	A A A A	a_j	$6u$
2	B A A A	b_{1j}	$3u+3v-(l-m)\,\omega_{1j}$
3	A B A A	b_{2j}	$3u+3v-(l-m)\,\omega_{2j}$
4	A A B A	b_{3j}	$3u+3v-(l-m)\,\omega_{3j}$
5	A B B A	c_{1j}	$u+4v+w-\{(1/2)(l+n)-m\}\{\beta_1{}^2-(1/3)\}+\epsilon_{1j}(l-n)\beta_2\beta_3$
6	B A B A	c_{2j}	$u+4v+w-\{(1/2)(l+n)-m\}\{\beta_2{}^2-(1/3)\}+\epsilon_{2j}(l-n)\beta_3\beta_1$
7	B B A A	c_{3j}	$u+4v+w-\{(1/2)(l+n)-m\}\{\beta_3{}^2-(1/3)\}+\epsilon_{3j}(l-n)\beta_1\beta_2$
8	B B B A	d_j	$3v+3w+(m-n)\omega_j$
9	A A A B	e_j	$3u+3v-(l-m)\omega_j$
10	B A A B	f_{1j}	$u+4v+w-\{(1/2)(l+n)-m\}\{\beta_1{}^2-(1/3)\}-\epsilon_{1j}(l-n)\beta_2\beta_3$
11	A B A B	f_{2j}	$u+4v+w-\{(1/2)(l+n)-m\}\{\beta_2{}^2-(1/3)\}-\epsilon_{2j}(l-n)\beta_3\beta_1$
12	A A B B	f_{3j}	$u+4v+w-\{(1/2)(l+n)-m\}\{\beta_3{}^2-(1/3)\}-\epsilon_{3j}(l-n)\beta_1\beta_2$
13	A B B B	g_{1j}	$3v+3w+(m-n)\omega_{1j}$
14	B A B B	g_{2j}	$3v+3w+(m-n)\omega_{2j}$
15	B B A B	g_{3j}	$3v+3w+(m-n)\omega_{3j}$
16	B B B B	h_j	$6w$

of a qudruplet may be occupied by A or B atoms as shown in the second column of Table 1. Thus, we have 64 kinds of quadruplets, which are generally not equivalent to each other when the directional order occurs. The numbers of the quadruplets are defined by a_j's, b_{ij}'s, c_{ij}'s, d_j's, e_j's, f_{ij}'s, g_{ij}'s, and h_j's, as shown in the third column of Table 1, where $j=1, 2, 3$, and 4 corresponding to the group i, ii, iii, and iv, respectively, and $i=1, 2$, and 3.

The above-introduced order parameters r_j, a_j, b_{ij}, c_{ij}, d_j, e_j, f_{ij}, g_{ij}, and h_j ($i=1, 2, 3$; $j=1, 2, 3,4$) are not all independent, and there are following restrictions :—— The condition that the total number of A atoms is $N/4$ can be expressed as

$$\sum_{i=1}^{3}\{(1-r_i)/3\}+r_4=1\ , \tag{2}$$

and

$$4a_j+\sum_{i=1}^{3}(3b_{ij}+2c_{ij})+d_j+3e_j+\sum_{i=1}^{3}(2f_{ij}+g_{ij})=1 \tag{3}$$
$$(j=1,\ 2,\ 3,\ \text{and}\ 4)\ .$$

Also, from the conditions that the numbers of the quadruplets belonging to the i, ii, iii, and iv groups are all equal to $N/4$, we have

$$a_j+\sum_{i=1}^{3}(b_{ij}+c_{ij})+d_j+e_j+\sum_{i=1}^{3}(f_{ij}+g_{ij})+h_j=1 \tag{4}$$
$$(j=1,\ 2,\ 3,\ \text{and}\ 4)\ .$$

Finally, taking a count of the numbers of A atoms on the sublattices I, II, and III, we have

$$\left.\begin{aligned}(1-r_1)/3&=a_j+b_{2j}+b_{3j}+c_{1j}+e_j+f_{2j}+f_{3j}+g_{1j}\ ,\\ (1-r_2)/3&=a_j+b_{3j}+b_{1j}+c_{2j}+e_j+f_{3j}+f_{1j}+g_{2j}\ ,\\ \text{and}\quad (1-r_3)/3&=a_j+b_{1j}+b_{2j}+c_{3j}+e_j+f_{1j}+f_{2j}+g_{3j}\ ,\\ &(j=1,\ 2,\ 3,\ \text{and}\ 4)\ .\end{aligned}\right\} \tag{5}$$

III. Quasi-chemical equations and the minimization of the free energy

1. Internal energy of the system

In the following, the case of magnetic annealing will be considered. It is supposed that the directional order of atoms is so produced that the free energy of the system including the ferromagnetic anisotoropy energy may be minimized at the mangetic annealing temperature. Let the direction cosines of the intrinsic magnetization referred to the tetragonal axes be denoted by β_i ($i=1,\ 2,\ 3$) and the angle between the direction of an atom pair and that of the intrinsic magnetization be denoted by ϕ. It may be assumed that the energies of the atom pairs AA, AB, and BB along any nearest-neighbor directions, E_{AB}, E_{AA}, and E_{BB}, are expressed as

$$E_{AA}=u+l\{\cos^2\phi-(1/3)\}\ ,\ E_{AB}=v+m\{\cos^2\phi-(1/3)\}\ ,$$

and $$E_{BB} = w + n\left\{\cos^2\phi - (1/3)\right\}\ , \tag{6}$$

respectively. Then, the summation of the pair energies according to various manners of quadruplets yields the energies of quadruplets, which are given in the fourth column of Table 1, where abbreviations

$$\left.\begin{aligned} \omega_1 &= \omega_{32} = \omega_{13} = \omega_{24} = \beta_2\beta_3 + \beta_3\beta_1 + \beta_1\beta_2\ , \\ \omega_2 &= \omega_{31} = \omega_{23} = \omega_{14} = -\beta_2\beta_3 - \beta_3\beta_1 + \beta_1\beta_2\ , \\ \omega_3 &= \omega_{11} = \omega_{22} = \omega_{34} = \beta_2\beta_3 - \beta_3\beta_1 - \beta_1\beta_2\ , \\ \omega_4 &= \omega_{21} = \omega_{12} = \omega_{33} = -\beta_2\beta_3 + \beta_3\beta_1 - \beta_1\beta_2\ , \end{aligned}\right\} \tag{7}$$

$$\left.\begin{aligned} &\epsilon_{11} = \epsilon_{21} = \epsilon_{31} = \epsilon_{32} = \epsilon_{13} = \epsilon_{24} = 1\ , \\ \text{and}\quad &\epsilon_{12} = \epsilon_{22} = \epsilon_{23} = \epsilon_{33} = \epsilon_{14} = \epsilon_{34} = -1 \end{aligned}\right\} \tag{8}$$

are used.

The internal energy, U, of the system as the sum of the energies of quadruplets is given, by using the geometrical relations (3), (4), and (5) and by omitting constant terms, as follows:

$$\begin{aligned} U = {} & (NV/4)\left\{3\sum_{j=1}^{4}(a_j + h_j) - \sum_{j=1}^{4}\sum_{i=1}^{3}(c_{ij} + f_{ij})\right\} \\ & - (NL/4)\left[\sum_{j=1}^{4}\left\{(d_j + e_j)\,\omega_j\right\} + \sum_{j=1}^{4}\sum_{i=1}^{3}\left[(b_{ij} + g_{ij})\,\omega_{ij} + (c_{ij} + f_{ij})\left\{\beta_i^2 - (1/3)\right\}\right]\right], \end{aligned} \tag{9}$$

where $$V = (1/2)\,(u + w) - v \tag{10}$$

and $$L = (1/2)\,(l + n) - m\ . \tag{11}$$

In Eq. (9), the first term is the formation energy of the superlattice, and the second one expresses the ferromagnetic anisotropy energy responsible for the directional order.

2. Quasi-chemical equations

For given r_i's, a_j's, b_{ij}'s, c_{ij}'s, d_j's, e_j's, f_{ij}'s, g_{ij}'s, and h_j's, the normalized number of configurations, G, is written as:——

$$\begin{aligned} G\,(r_i\text{'s};\ a_j\text{'s},\ b_{ij}\text{'s},\ \cdots,\ h_j\text{'s}) = {} & \frac{(N/4)\,!}{\left\{(N/4)\sum_{i=1}^{3}(r_i/3)\right\}!\left[(N/4)\left\{1-\sum_{i=1}^{3}(r_i/3)\right\}\right]!} \\ & \times\prod_{i=1}^{3}\frac{(N/4)\,!}{\left\{(N/4)\,(1-r_i)/3\right\}!\left\{(N/4)\,(2+r_i)/3\right\}!} \\ & \times\prod_{j=1}^{4}\frac{(Na_j{}^*/4)!\,(Nd_j{}^*/4)!\,(Ne_j{}^*/4)!\,(Nh_j{}^*/4)!}{(Na_j/4)!\,(Nd_j/4)!\,(Ne_j/4)!\,(Nh_j/4)!} \\ & \times\prod_{j=1}^{4}\prod_{i=1}^{3}\frac{(Nb_{ij}{}^*/4)!\,(Nc_{ij}{}^*/4)!\,(Nf_{ij}{}^*/4)!\,(Ng_{ij}{}^*/4)!}{(Nb_{ij}/4)!\,(Nc_{ij}/4)!\,(Nf_{ij}/4)!\,(Ng_{ij}/4)!}\ , \end{aligned} \tag{12}$$

where a_j*'s, b_{ij}*'s, ..., and h_j*'s denote respectively the values of a_j's, b_{ij}'s, ..., and h_j's for a completely random arrangement under fixed r_i's. Thus a_j*'s, b_{ij}*'s, ..., and h_j*'s may be determined, by maximizing

$$\Big[\prod_{j=1}^{4}\{(Na_j/4)!\,(Nd_j/4)!\,(Ne_j/4)!\,(Nh_j/4)!\}\cdot\prod_{j=1}^{4}\prod_{i=1}^{3}\{(Nb_{ij}/4)!\,(Nc_{ij}/4)!\times(Nf_{ij}/4)!\,(Ng_{ij}/4)!\}\Big]^{-1}$$

under the subsidiary conditions (3), (4), and (5), as

$$\left.\begin{aligned}
a_j^* &= (1/3^4)\sum_{k=1}^{3} r_k\cdot\prod_{k=1}^{3}(1-r_k)\ ,\\
b_{ij}^* &= (1/3^4)\sum_{k=1}^{3} r_k\cdot\prod_{k=1}^{3}(1-r_k)\cdot(2+r_i)/(1-r_i)\ ,\\
c_{ij}^* &= (1/3^4)\sum_{k=1}^{3} r_k\cdot\prod_{k=1}^{3}(2+r_k)\cdot(1-r_i)/(2+r_i)\ ,\\
d_j^* &= (1/3^4)\sum_{k=1}^{3} r_k\cdot\prod_{k=1}^{3}(2+r_k)\ ,\\
e_j^* &= (1/3^4)(3-\sum_{k=1}^{3} r_k)\cdot\prod_{k=1}^{3}(1-r_k)\ ,\\
f_{ij}^* &= (1/3^4)(3-\sum_{k=1}^{3} r_k)\cdot\prod_{k=1}^{3}(1-r_k)\cdot(2+r_i)/(1-r_i)\ ,\\
g_{ij}^* &= (1/3^4)(3-\sum_{k=1}^{3} r_k)\cdot\prod_{k=1}^{3}(2+r_k)\cdot(1-r_i)/(2+r_i)\ ,\\
\text{and}\quad h_j^* &= (1/3^4)(3-\sum_{k=1}^{3} r_k)\cdot\prod_{k=1}^{3}(2+r_k)\ ,\\
&\quad (i=1,2,3;\ j=1,2,3,4)\ .
\end{aligned}\right\}\qquad(13)$$

The configurational partition function, Ω, as a function of the temperature, T, and anisotropic long-range order parameters, r_i's, is obtained by substituting Eqs. (9) and (12) in the general formula

$$\Omega(T, r_i\text{'s}) = \sum G(r_i\text{'s}; a_j\text{'s}, b_{ij}\text{'s}, \cdots, h_j\text{'s})\exp\{-U(r_i\text{'s}; a_i\text{'s}, b_{ij}\text{'s}, \cdots, h_j\text{'s})/kT\}\ ,\qquad(14)$$

where the summation extends over all values of a_j's, b_{ij}'s, $\cdots$, and h_j's which are consistent with the subsidiary conditions (3), (4), and (5). As usual, the sum in Eq. (14) may be replaced by its maximum term, and thus we have

$$\Omega(T, r_i\text{'s}) = G(r_i\text{'s}; a_j\text{'s}, b_{ij}\text{'s}, \cdots, h_j\text{'s})\exp\{-U(r_i\text{'s}; a_j\text{'s}, b_{ij}\text{'s}, \cdots, h_j\text{'s})/kT\}\ .\qquad(15)$$

It should be noticed that a_j's, b_{ij}'s, $\cdots$, and h_j's in Eq. (15) and in the following expressions are such as to maximize Eq. (15) under the subsidiary conditions (3), (4), and (5). The conditions of this maximization are as follows:——

$$\left.\begin{aligned}
\ln(a_j^2\, d_j/b_{1j}\, b_{2j}\, b_{3j}) &= -(6V/kT) + (2L/kT)\,\omega_j\ ,\\
\ln(e_j\, h_j^2/g_{1j}\, g_{2j}\, g_{3j}) &= -(6V/kT) + (2L/kT)\,\omega_j\ ,
\end{aligned}\right.$$

$$\left.\begin{aligned}
&\ln(a_j h_j/b_{ij} g_{ij}) = -(6V/kT) - (2L/kT)\,\omega_{ij}\ ,\\
&\ln(a_j c_{ij} b_{ij}/b_{1j} b_{2j} b_{3j}) = -(2V/kT)\\
&\qquad + (L/3kT)\left\{3\beta_i^2 + 6\epsilon_{ij}(\beta_1\beta_2\beta_3/\beta_i) - 1\right\}\ ,\\
\text{and}\quad &\ln(f_{ij} h_j g_{ij}/g_{1j} g_{2j} g_{3j}) = -(2V/kT)\\
&\qquad + (L/3kT)\left\{3\beta_i^2 + 6\epsilon_{ij}(\beta_1\beta_2\beta_3/\beta_i) - 1\right\}\ ,\\
&(i = 1, 2, 3;\ j = 1, 2, 3, 4)\ .
\end{aligned}\right\} \tag{16}$$

These are the so-called quasi-chemical equations.

3. Minimum conditions for the free energy

The free energy for any value of T and r_i's is given by

$$F = -kT\ln\Omega(T,\ r_i\text{'s}) = -kT\ln G(r_i\text{'s}) + U(r_i\text{'s})\ . \tag{17}$$

Minimizing the free energy for a fixed temperature, T, we obtain eventually

$$\left.\begin{aligned}
&\ln\left\{(1-r_1)\left(3-\sum_{i=1}^{3} r_i\right)/(2+r_1)\sum_{i=1}^{3} r_i\right\} - (1/3)\sum_{j=1}^{4}\ln(f_{3j}/c_{2j})\\
&\qquad = (4L/3kT)(\beta_2^2 - \beta_3^2)\ ,\\
&\ln\left\{(1-r_2)\left(3-\sum_{i=1}^{3} r_i\right)/(2+r_2)\sum_{i=1}^{3} r_i\right\} - (1/3)\sum_{j=1}^{4}\ln(f_{1j}/c_{3j})\\
&\qquad = (4L/3kT)(\beta_3^2 - \beta_1^2)\ ,\\
\text{and}\quad &\ln\left\{(1-r_3)\left(3-\sum_{i=1}^{3} r_i\right)/(2+r_3)\sum_{i=1}^{3} r_i\right\} - (1/3)\sum_{j=1}^{4}\ln(f_{2j}/c_{1j})\\
&\qquad = (4L/3kT)(\beta_1^2 - \beta_2^2)\ .
\end{aligned}\right\} \tag{18}$$

Thus the equilibrium values of the order parameters r_i's, a_j's, b_{ij}'s, $\cdots$, and h_j's can be determined from the simultaneous equations (3), (4), (5), (16), and (18).

For a non-ferromagnetic solution ($L=0$), we can put as

$$r_i = r;\ a_j = a,\ b_{ij} = b,\ c_{ij} = c,\ \cdots,\ \text{and}\ h_j = h;\ (i = 1, 2, 3;\ j = 1, 2, 3, 4)\ . \tag{19}$$

Then, equations (3), (4), (5), (16), and (18) are reduced respectively to

$$\left.\begin{aligned}
&4a + 9b + 6c + d + 3e + 6f + 3g = 1\ ,\\
&a + 3b + 3c + d + e + 3f + 3g + h = 1\ ,\\
&a + 2b + c + e + 2f + g = (1-r)/3\ ,\\
&\ln(a^2 d/b^3) = -6V/kT\ ,\\
&\ln(eh^2/g^3) = -6V/kT\ ,\\
&\ln(ah/bg) = -6V/kT\ ,\\
&\ln(ac/b^2) = -2V/kT\ ,\\
&\ln(fh/g^2) = -2V/kT\ ,\\
\text{and}\quad &\ln\left\{(1-r)^2/r(2+r)\right\} - (4/3)\ln(f/c) = 0\ ,
\end{aligned}\right\} \tag{20}$$

which coincide exactly with the result of McGlashan's theory[16] developed for the AB_3–type superlattice.

IV. Approximate calculation of the order parameters

Since it is difficult to exactly solve the simultaneous equations (3), (4), (5), (16), and (18), the method of successive approximation is used. Using the parameters determined from Eqs. (20) as the zeroth approximation, we put

$$\left.\begin{aligned} &r_i = r + r_i' \,; \\ &a_j = a + a_j',\ b_{ij} = b + b_{ij}',\ c_{ij} = c + c_{ij}',\ d_j = d + d_j' \,, \\ &e_j = e + e_j',\ f_{ij} = f + f_{ij}',\ g_{ij} = g + g_{ij}',\ \text{and}\ h_j = h + h_j' \,; \\ &\quad (i = 1, 2, 3\,; j = 1, 2, 3, 4) \,. \end{aligned}\right\} \tag{21}$$

Since the degree of the directional order developed in actual cases is very small,[14] it may hold that, under normal conditions,

$$\left.\begin{aligned} &|r_i'/r| \ll 1\,;\ |a_j'/a| \ll 1,\ |b_{ij}'/b| \ll 1,\ |c_{ij}'/c| \ll 1,\ |d_j'/d| \ll 1, \\ &|e_j'/e| \ll 1,\ |f_{ij}'/f| \ll 1,\ |g_{ij}'/g| \ll 1,\ \text{and}\ |h_j'/h| \ll 1\,; \\ &\quad (i = 1, 2, 3\,; j = 1, 2, 3, 4) \,. \end{aligned}\right\} \tag{22}$$

With the help of relations (21) and (22) together with Eqs. (20), the quasi-chemical eqations (16) are reduced to

$$\left.\begin{aligned} &\frac{c_{ij}'}{c} = -\frac{a_j'}{a} - \frac{b_{ij}'}{b} + \sum_{i=1}^{3} \frac{b_{ij}'}{b} + \frac{L}{3kT}\left\{3\beta_i^2 + 6\epsilon_{ij}\frac{\beta_1\beta_2\beta_3}{\beta_i} - 1\right\}, \\ &\frac{d_j'}{d} = -2\frac{a_j'}{a} + \sum_{i=1}^{3} \frac{b_{ij}'}{b} + \frac{2L}{kT}\omega_j \,, \\ &\frac{e_j'}{e} = 3\frac{a_j'}{a} - \sum_{i=1}^{3} \frac{b_{ij}'}{b} + \frac{h_j'}{h} \,, \\ &\frac{f_{ij}'}{f} = 2\frac{a_j'}{a} + \frac{b_{ij}'}{b} - \sum_{i=1}^{3} \frac{b_{ij}'}{b} + \frac{h_j'}{h} \\ &\qquad\qquad + \frac{L}{3kT}\left\{3\beta_i^2 - 6\epsilon_{ij}\frac{\beta_1\beta_2\beta_3}{\beta_i} - 1\right\} \,, \\ &\text{and}\quad \frac{g_{ij}'}{g} = \frac{a_j'}{a} - \frac{b_{ij}'}{b} + \frac{h_j'}{h} + \frac{2L}{kT}\omega_{ij} \\ &\quad (i = 1, 2, 3\,; j = 1, 2, 3, 4) \,, \end{aligned}\right\} \tag{23}$$

and hence the geometrical relations (3), (4), and (5) are reduced to

$$x_1\frac{a_j'}{a} + x_2\sum_{i=1}^{3}\frac{b_{ij}'}{b} + 3x_3\frac{h_j'}{h} + \frac{2L}{kT}x_4\omega_j = 0 \,,$$

(16) M.L. McGlashan : Thesis (1951), Reading University, quoted in E. A. Guggenheim ; *Mixtures*,Oxford U.P., Oxford (1952), p. 137.

$$y_1\frac{a_j'}{a}+y_2\sum_{i=1}^{3}\frac{b_{ij}'}{b}+y_3\frac{h_j'}{h}+\frac{2L}{kT}y_4\omega_j=0\ ,$$

and
$$r_i'+3z_1\frac{a'_j}{a}+3z_2\frac{b_{ij}'}{b}+3z_3\sum_{i=1}^{3}\frac{b_{ij}'}{b}+3x_3\frac{h_j'}{h}+\frac{L}{kT}z_4\left\{3\beta_i^2+6\epsilon_{ij}\frac{\beta_1\beta_2\beta_3}{\beta_i}-1\right\}+\frac{6L}{kT}z_5\omega_{ij}=0\ ,$$

$$(i=1,2,3\,;\,j=1,2,3,4) \tag{24}$$

with abbreviations

$$\begin{aligned}
&x_1=4a-6c-2d+9e+12f+3g\,, && x_2=3b+4c+d-3e-4f-g\,,\\
&x_3=e+2f+g\,, && x_4=2c+d-2f-g\,,\\
&y_1=a-3c-2d+3e+6f+3g\,, && y_2=b+2c+d-e-2f-g\,,\\
&y_3=e+3f+3g+h\,, && y_4=c+d-f-g\,,\\
&z_1=a-c+3e+4f+g\,, && z_2=-b-c-f-g\,,\\
&z_3=b+c-e-f\,, && z_4=c-f\,,
\end{aligned} \tag{25}$$

and $z_5=f+g$.

Similary, Eqs. (18) become

$$\frac{9}{(1-r)(2+r)}r_i'+\frac{1}{r(1-r)}\sum_{i=1}^{3}r_i'+\sum_{j=1}^{4}\left(3\frac{a_j'}{a}-\frac{b_{ij}'}{b}-\sum_{i=1}^{3}\frac{b_{ij}'}{b}+\frac{h'_j}{h}\right)=0 \tag{26}$$

$$(i=1,2,3)\ .$$

Solving the simultaneous equations (24) and (26) and using Eqs. (23), we obtain

$$\begin{aligned}
&r_i'=(2L/kT)\,R\left\{\beta_i^2-(1/3)\right\}\,;\\
&a_j'=(2L/kT)\,a\,A\,\omega_j\ ,\\
&b_{ij}'=(2L/kT)b\left[B_1\left\{\beta_i^2-(1/3)\right\}+B_2\omega_{ij}+B_3\epsilon_{ij}(\beta_1\beta_2\beta_3/\beta_i)\right]\ ,\\
&c_{ij}'=(2L/kT)c\left[C_1\left\{\beta_i^2-(1/3)\right\}+C_2\omega_{ij}+C_3\epsilon_{ij}(\beta_1\beta_2\beta_3/\beta_i)\right]\ ,\\
&d_j'=(2L/kT)\,d\,D\omega_j\ ,\\
&e_j'=(2L/kT)\,e\,E\omega_j\ ,\\
&f_{ij}'=(2L/kT)f\left[F_1\left\{\beta_i^2-(1/3)\right\}+F_2\omega_{ij}+F_3\epsilon_{ij}(\beta_1\beta_2\beta_3/\beta_i)\right]\ ,\\
&g_{ij}'=(2L/kT)\,g\left[G_1\left\{\beta_i^2-(1/3)\right\}+G_2\omega_{ij}+G_3\epsilon_{ij}(\beta_1\beta_2\beta_3/\beta_i)\right]\ ,\\
&\text{and}\quad h_j'=(2L/kT)\,h\,H\,\omega_j\,;\ (i=1,2,3;\ j=1,2,3,4)\ ,
\end{aligned} \tag{27}$$

where

$$R=-6(1-r)(2+r)\,z_4\{4(1-r)(2+r)+27z_2\}^{-1}\,,$$

$$
\begin{aligned}
A &= [3x_3y_4-x_4y_3-(x_2y_3-3x_3y_2)\{-3x_3(x_1y_4-x_4y_1)+3z_1(3x_3y_4-x_4y_3)\\
&\quad+(z_4-z_5)(x_1y_3-3x_3y_1)\}\{3x_3(x_1y_2-x_2y_1)+3z_1(x_2y_3-3x_3y_2)\\
&\quad+(x_3-2z_3)(x_1y_3-3x_3y_1)\}^{-1}](x_1y_3-3x_3y_1)^{-1},\\
B_1 &= -(27/2)z_4\{4(1-r)(2+r)+27z_2\}^{-1},\\
B_2 &= [-(x_1y_3-3x_3y_1)\{x_3z_5-z_3(z_4+z_5)\}+z_2\{x_3(x_1y_4-x_4y_1)-z_1(3x_3y_4-x_4y_3)\}\\
&\quad-(z_4+2z_5)\{x_3(x_1y_2-x_2y_1)+z_1(x_2y_3-3x_3y_2)\}]z_2^{-1}\{3x_3(x_1y_2-x_2y_1)\\
&\quad+3z_1(x_2y_3-3x_3y_2)+(x_3-2z_3)(x_1y_3-3x_3y_1)\}^{-1},\\
B_3 &= [-(x_1y_3-3x_3y_1)(x_3z_4-2z_3z_5)-2z_2\{x_3(x_1y_4-x_4y_1)-z_1(3x_3y_4-x_4y_3)\}\\
&\quad-(z_4+2z_5)\{x_3(x_1y_2-x_2y_1)+z_1(x_2y_3-3x_3y_2)\}]z_2^{-1}\{3x_3(x_1y_2-x_2y_1)\\
&\quad+3z_1(x_2y_3-3x_3y_2)+(x_3-2z_3)(x_1y_3-3x_3y_1)\}^{-1},\\
H &= [-x_1y_4+x_4y_1-(x_1y_2-x_2y_1)\{-3x_3(x_1y_4-x_4y_1)+3z_1(3x_3y_4-x_4y_3)\\
&\quad+(z_4-z_5)(x_1y_3-3x_3y_1)\}\{3x_3(x_1y_2-x_2y_1)+3z_1(x_2y_3-3x_3y_2)\\
&\quad+(x_3-2z_3)(x_1y_3-3x_3y_1)\}^{-1}](x_1y_3-3x_3y_1)^{-1},
\end{aligned}
$$

$$
\begin{aligned}
&C_1=(1/2)-B_1,\ C_2=A-B_3,\ C_3=1-2A-2B_2+B_3,\\
&D=1-2A-B_2+B_3,\ E=3A+B_2-B_3+H,\\
&F_1=(1/2)+B_1,\ F_2=-2A+B_3-H,\ F_3=-1+4A+2B_2-B_3+2H,\\
&G_1=-B_1,\ G_2=1-A-B_2-H,\ \text{and}\ G_3=2A-B_3+2H.
\end{aligned}
\tag{28}
$$

According to Eqs. (27), we obtain $\sum_{i=1}^{3} r_i'=0$, $\sum_{j=1}^{4} a_j'=0$, $\sum_{j=1}^{4}\sum_{i=1}^{3} b_{ij}'=0$, $\sum_{j=1}^{4}\sum_{i=1}^{3} c_{ij}'=0$, $\sum_{j=1}^{4} d_j'=0$, $\sum_{j=1}^{4} e_j'=0$, $\sum_{j=1}^{4}\sum_{i=1}^{3} f_{ij}'=0$, $\sum_{j=1}^{4}\sum_{i=1}^{3} g_{ij}'=0$, and $\sum_{j=1}^{4} h_j'=0$, which indicate that the gravity centers of r_i's, a_j's, b_{ij}'s, $\cdots$, and h_j's do not suffer any change by magnetic annealing. Eqs. (28) together with Eqs. (25) show that R, A, B_i, C_i, D, E, F_i, G_i, and H ($i=1, 2, 3$) are explicit functions of the order parameters in zeroth approximation, r, a, b, c, d, e, f, g, and h, which can be determined from Eqs. (20). Thus, the equilibrium values of order parameters r_i's, a_j's, b_{ij}'s, $\cdots$, and h_j's can be calculated numerically as functions of the temperature.

Numerical calculations of the order parameters have been made for the case that V is positive or the order-disorder transition occurs, under the assumptions that V and L are independent of the temperature. The equilibrium values of r, a, b, $\cdots$, and h as function of the temperature are shown in Fig. 3, which indicates that the critical temperature, T_c, of the order-disorder transition is $0.4112\times 2V/k$. For the sake of convenience in later considerations, a short-range order

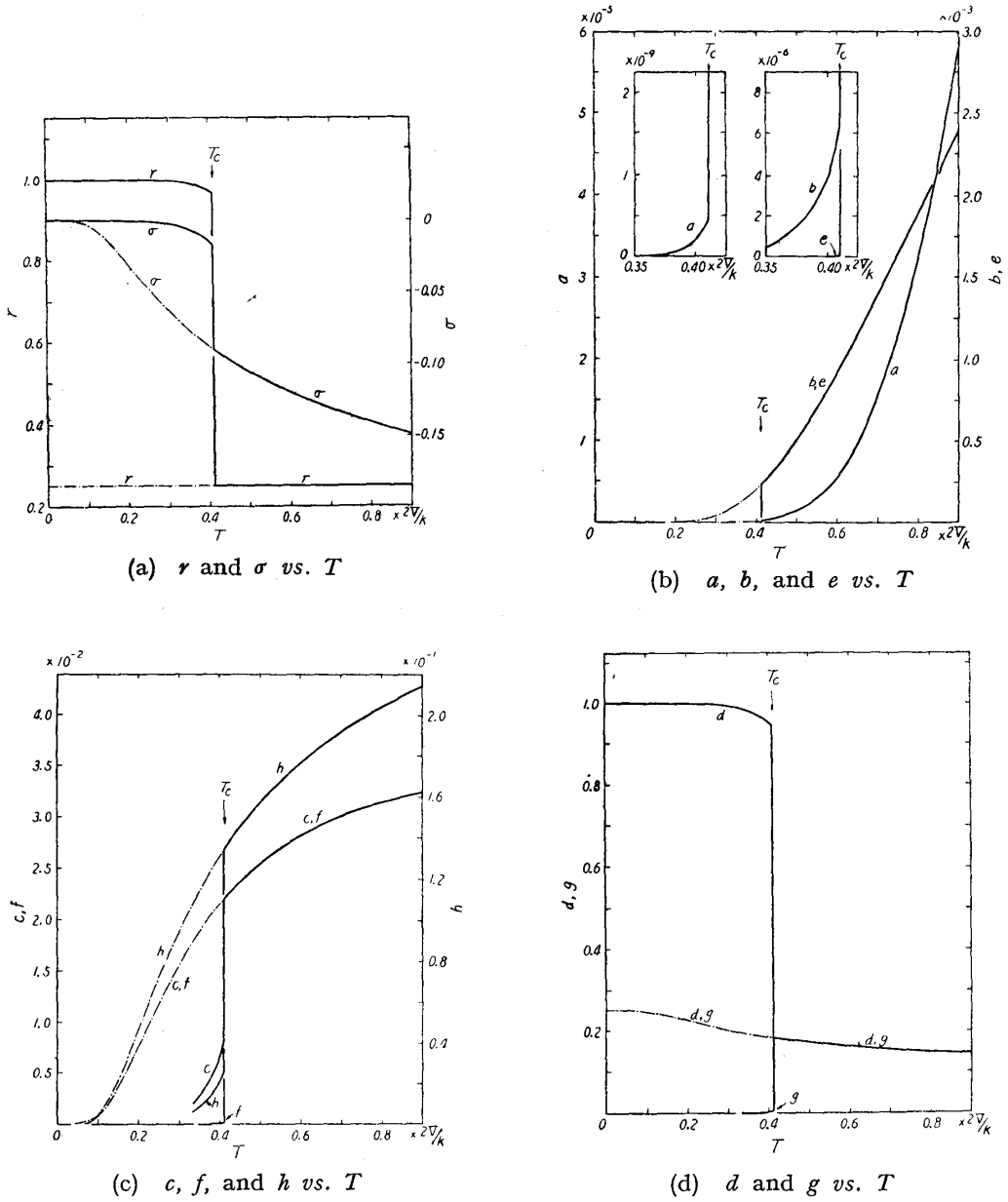


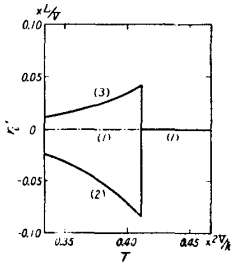
Fig. 3. Equilibrium values of the order parameters, r, σ, a, b, c, d, e, f, g, and h, as dependent on the annealing temperature T, the critical temperature of the order-disorder transition being indicated by $T_c=0.4112\times 2V/k$. Chain curves express the equilibrium values of the parameters for a hypothetical case where the long-range order is absent ($r=1/4$).

parameter σ, which is defined as the difference of the probability of unlike-atom pairs from that of like-atom pairs, that is,

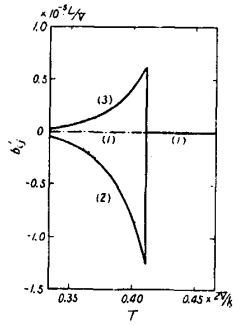
$$\sigma = -a + c + f - h \ , \tag{29}$$

is shown in Fig. 3 (a).

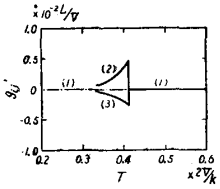
The equilibrium values of the induced parts of the order parameters, r_i', a_j', b_{ij}', $\cdots$, and h_j' ($i=$ 1, 2, 3 and $j=$1, 2, 3, 4) as dependent on the annealing temperature in the magnetic field applied along the [100], [110], and [111] directions are shown by solid curves in Figs. (4), (5), and (6), respectively. It is to be noted



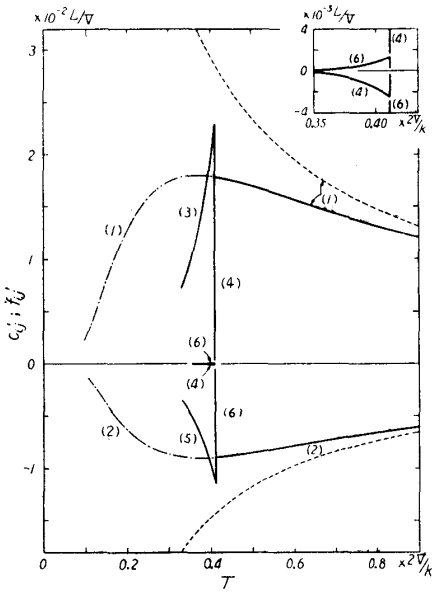
(a) (1) : r_i' $(i=1, 2, 3)$, (2) : r_1', (3) : r_2', r_3'



(b) (1) : b_{ij}' $(i=1, 2, 3;$ $j=1, 2, 3, 4)$, (2) : b_{1j}' $(j=1, 2, 3, 4)$, (3) : b_{2j}', b_{3j}' $(j=1, 2, 3, 4)$



(d) (1) : g_{ij}' $(i=1, 2, 3;$ $j=1, 2, 3, 4)$, (2) : g_{1j}' $(j=1, 2, 3, 4)$, (3) : g_{2j}', g_{3j}' $(j=1, 2, 3, 4)$

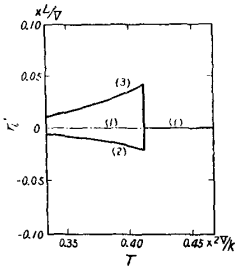


(c) (1) : c_{1j}'; f_{1j}' $(j=1, 2, 3, 4)$, (2) : c_{2j}', c_{3j}' ; f_{2j}', f_{3j}' $(j=1, 2, 3, 4)$, (3) : c_{1j}' $(j=1, 2, 3, 4)$, (4) : f_{1j}' $(j=1, 2, 3, 4)$, (5) : c_{2j}', c_{3j}' $(j=1, 2, 3, 4)$, (6) : f_{2j}', f_{3j}' $(j=1, 2, 3, 4)$

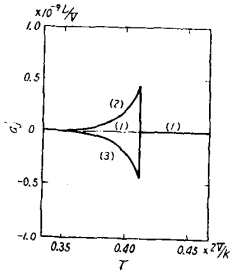
Fig. 4. Equilibrium values of the induced parts of the order parameters, r_i''s, b_{ij}''s, c_{ij}''s, f_{ij}''s, and g_{ij}''s, as dependent on the annealing temperature in the magnetic field applied along the [100] direction. Chain curves express the equilibrium values for a hypothetical case where the long-range order is absent $(r=1/4)$, and dashed curves express those for the ideal solution $(V=0)$. Parameters other than given in the figures are always zero.

that, in the case of mangetic annealing along the [100] direction, $a_j'=0$, $d_{ij}'=0$, $e_{ij}'=0$, and $h_{ij}'=0$, and in the case of magnetic annealing along the [111] direction, $r_i'=0$. In these figures, chain curves indicate the values for a hypothetical case where there is no development of the long-range order $(r=1/4)$. Further, the temperature dependence of the induced parts of the order parameters for the ideal solution $(V=0)$ is shown by dashed curves in the same figures, and in this case V in the scales of the ordinate and abscissa must be replaced by L. For the sake of mutual comparison of the curves for ideal and non-ideal solutions, however, there is no necessity for such a replacement, since, if we put into V in the scales for the ideal solution the same V value with that of the non-ideal solution with which we wish to make comparison, then the same values of abscissa and ordinate signify respectively the same annealing temperature and the same values of the order parameters for both kinds of solid solutions.

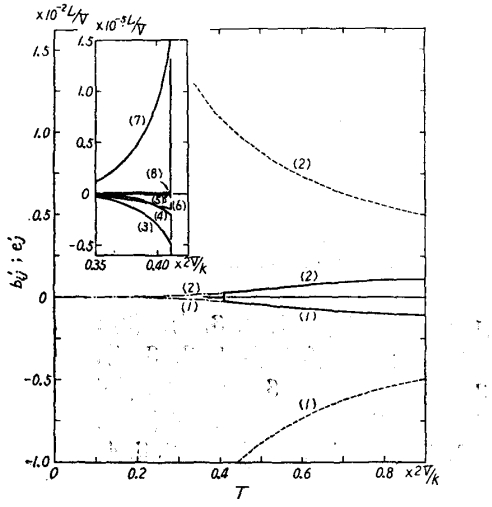
In the case of the [100] magnetic annealing (Fig. 4), as the annealing



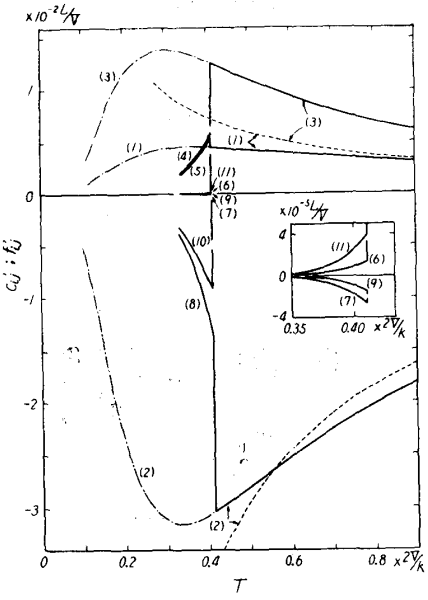
(a) (1) : r_i' (i=1, 2, 3), (2) : r_1', r_2', (3) : r_3'



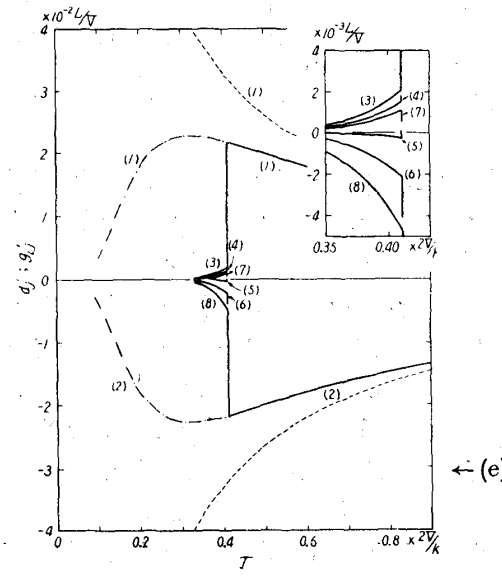
(b) (1) : a_j' (j=1, 2, 3, 4), (2) : a_1', a_2', (3) : a_3', a_4'



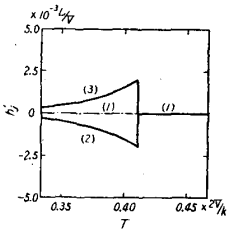
(c) (1) : b_{11}', b_{12}', b_{21}', b_{22}', b_{33}', b_{34}' ; e_3', e_4', (2) : b_{13}', b_{14}', b_{23}', b_{24}', b_{31}', b_{32}' ; e_1', e_2', (3) : b_{11}', b_{12}', b_{21}', b_{22}', (4) : b_{33}', b_{34}', (5) : e_3', e_4', (6) : b_{13}', b_{14}', b_{23}', b_{24}', (7) : b_{31}', b_{32}', (8) : e_1', e_2'



(d) (1) : c_{11}', c_{12}', c_{21}', c_{22}', c_{13}', c_{14}', c_{23}', c_{24}' ; f_{11}', f_{12}', f_{21}', f_{22}', f_{13}', f_{14}', f_{23}', f_{24}', (2) : c_{31}', c_{32}' ; f_{33}', f_{34}', (3) : c_{33}', c_{34}' ; f_{31}', f_{32}', (4) : c_{11}', c_{12}', c_{21}', c_{22}', (5) : c_{13}', c_{14}', c_{23}', c_{24}', (6) : f_{11}', f_{12}', f_{21}', f_{22}', (7) : f_{13}', f_{14}', f_{23}', f_{24}', (8) : c_{31}', c_{32}', (9) : f_{33}', f_{34}', (10) : c_{33}', c_{34}', (11) : f_{31}', f_{32}'

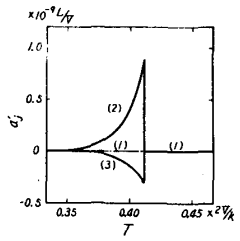


← (e) (1) : d_1', d_2' ; g_{13}', g_{14}', g_{23}', g_{24}', g_{31}', g_{32}', (2) : d_3', d_4' ; g_{11}', g_{12}', g_{21}', g_{22}', g_{33}', g_{34}', (3) : d_1', d_2', (4) : g_{13}', g_{14}', g_{23}', g_{24}', (5) : g_{31}', g_{32}', (6) : d_3', d_4', (7) : g_{11}', g_{12}', g_{21}', g_{22}', (8) : g_{33}', g_{34}'

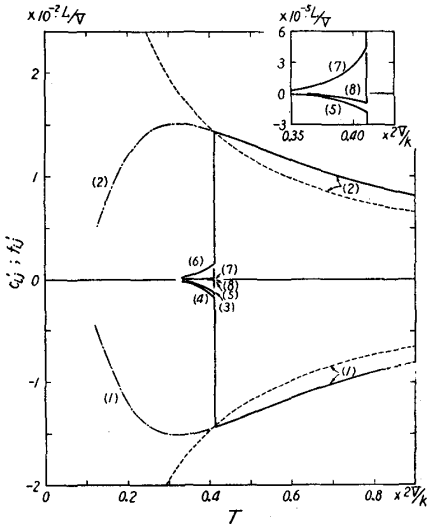


(f) (1) : h_j' (j=1, 2, 3, 4) , (2) : h_1', h_2', (3) : h_3', h_4'

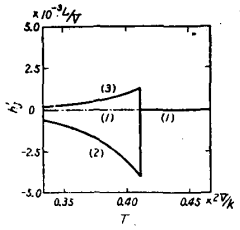
Fig. 5. Equilibrium values of the induced parts of the order parameters, r_i''s, a_j''s, b_{ij}''s, c_{ij}''s, d_j''s, e_j''s, f_{ij}''s, g_{ij}''s, and h_j''s, as dependent on the annealing temperature in the magnetic filed applied along the [110] direction. Chain curves express the equilibrium values for a hypothetical case where the long-range order is absent (r=1/4), and dashed cruves show those for the ideal solution (V=0). Parameters other than given in the figures are always zero.



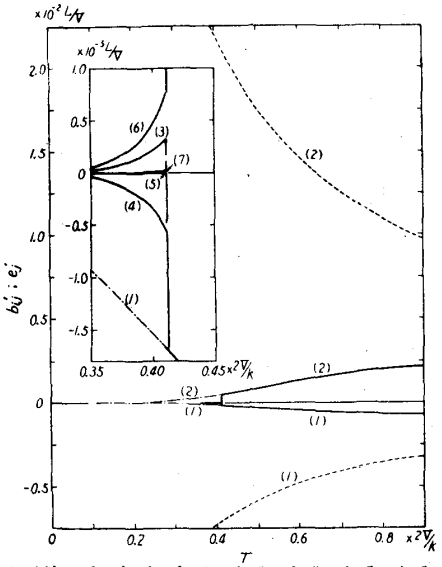
(a) (1) : a_j' (j=1, 2, 3, 4), (2) : a_1', (3) : a_2', a_3', a_4'



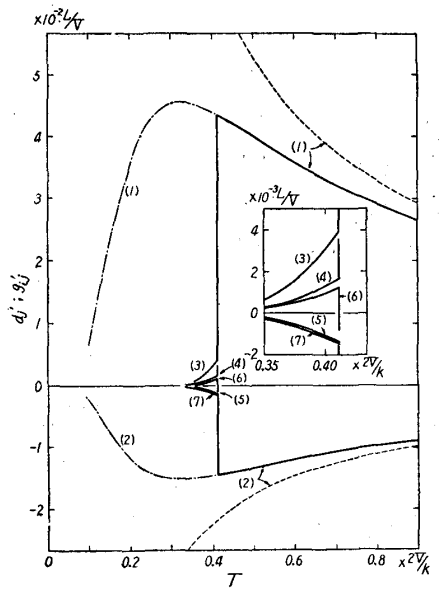
(c) (1) : c_{11}', c_{21}', c_{31}', c_{13}', c_{24}', c_{32}'; f_{12}', f_{14}', f_{22}', f_{23}', f_{33}', f_{34}', (2) : c_{12}', c_{14}', c_{22}', c_{23}', c_{33}', c_{34}'; f_{11}', f_{21}', f_{31}', f_{13}', f_{24}', f_{32}', (3) : c_{11}', c_{21}', c_{31}', (4) : c_{13}', c_{24}', c_{32}', (5) : f_{12}', f_{14}', f_{22}', f_{23}', f_{33}', f_{34}', (6) : c_{12}', c_{14}', c_{22}', c_{23}', c_{33}', c_{34}', (7) : f_{11}', f_{21}', f_{31}', (8) : f_{13}', f_{24}', f_{32}'



(e) (1) : h_j' (j=1, 2, 3, 4), (2) : h_1', (3) : h_2', h_3', h_4'



(b) (1) : b_{11}', b_{21}', b_{31}', b_{12}', b_{14}', b_{22}', b_{23}', b_{33}', b_{34}'; e_2', e_3', e_4', (2) : b_{13}', b_{24}', b_{32}'; e_1', (3) : b_{11}', b_{21}', b_{31}', (4) : b_{12}', b_{14}', b_{22}', b_{23}', b_{33}', b_{34}', (5) : e_2', e_3', e_4', (6) : b_{13}', b_{24}', b_{32}', (7) : e_1'



(d) (1) : d_1'; g_{13}', g_{24}', g_{32}', (2) : d_2', d_3', d_4'; g_{11}', g_{21}', g_{31}', g_{12}', g_{14}', g_{22}', g_{23}', g_{33}', g_{34}', (3) : d_1', (4) : g_{13}', g_{24}', g_{32}', (5) : d_2', d_3', d_4', (6) : g_{11}', g_{21}', g_{31}', (7) : g_{12}', g_{14}', g_{22}', g_{23}', g_{33}', g_{34}'

Fig. 6. Equilibirium values of the induced parts of the order parameters, a_j''s, b_{ij}''s, c_{ij}''s, d_j''s, e_j''s, f_{ij}''s, g_{ij}''s, and h_j''s, as dependent on the annealing temperature in the magnetic field applied along the [111] direction. Chain curves express the equilibrium values for a hypothetical case where the long-range order is absent (r=1/4), and dashed curves show those parameters for the ideal solution (V=0). Parameters other than given in the figures are always zero.

temperature is decreased, r_i''s take finite values suddenly at the critical temperature, T_c, of the order-disorder transition, r'_1 and $r_2'=r_3'$ taking negative and positive values, respectively. Below this temperature, r_1' increases and $r_2'=r_3'$ decrease with decreasing annealing temperature (Fig. 4(a)). As Fig. 4(b) and (d) show, b_{ij}''s and g_{ij}''s take behaviors similar to r_i''s. Absolute values of c_{ij}''s and f_{ij}''s take finite values less than those for the ideal solution above T_c (Fig. 4(c)). The absolute values of c_{ij}''s show discontinuous increases at T_c and subsequent decreases, and f_{ij}''s change their signs through T_c. Other parameters suffer no change by the [100] magnetic annealing. In the case of the [110] magnetic annealing (Fig. 5), $r_1'=r_2'$ and r_3' take respectively negative and positive values suddenly at T_c (Figs. 5 (a)). In contrast with these, r_i''s are always zero in the case of the [111] magnetic annealing. Other parameters a_j''s, b_{ij}''s,$\cdots$, and h_j''s show such complicated behaviors as shown in Fig. 5(b)$\sim$(f) and Fig. 6(a)$\sim$(e).

V. Ferromagnetic anisotropy associated with the directional order

Till now the parameters r_i, a_j, b_{ij},$\cdots$, and h_j ($i=1, 2, 3$; $j=1, 2, 3, 4$) characterizing the atomic configuration have been considered. Next, we calculate the ferromagnetic anisotropy energy associated with the directional order, which is the orientation-dependent part of the internal energy of the system. Let us suppose that the ferromagnetic anisotropy energy is measured at temperature T' to which the directional order was quenched from a higher magnetic annealing temperature, T. Then, in the second term of Eq. (9), quantities L and β_i's (or ω_j's and ω_{ij}'s) are replaced by the corresponding ones at T', that is, by L' and β_i''s (or ω_j''s and ω_{ij}'s), respectively, and values given by Eqs. (21) and (27) are substituted for b_{ij}'s, c_{ij}'s,$\cdots$, and g_{ij}'s. Thus, for single crystal alloys, the associated ferromagnetic anisotropy energy, K, is given by

$$K=-k_1\sum_i \beta_i^2\beta_i'^2-k_2\sum_{i>j}\beta_i\beta_j\beta_i'\beta_j' \ , \tag{30}$$

where
$$k_1=2\,(cC_1+fF_1)\,NLL'/kT$$
and
$$k_2=2\,\{b(3B_2+B_3)+dD+eE+g\,(3G_2+G_3)\}\,NLL'/kT \ . \tag{31}$$

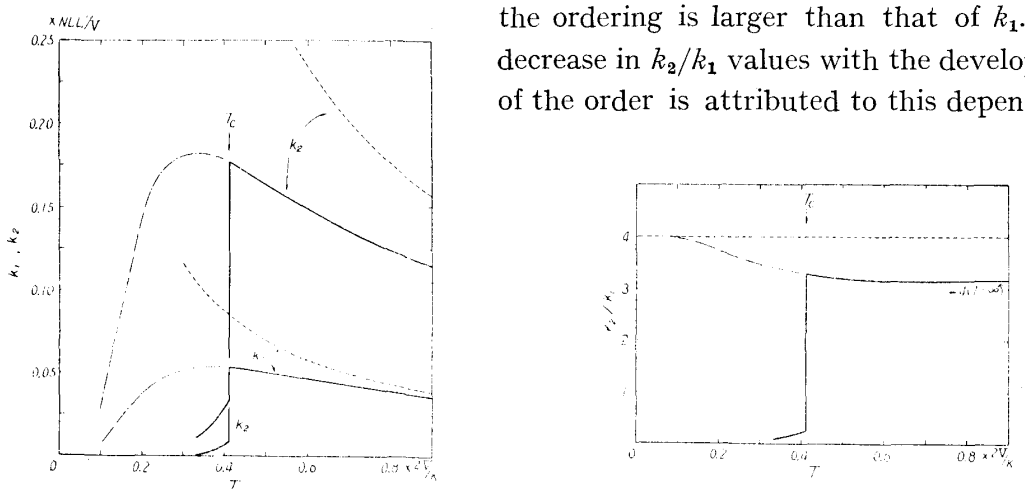
For the polycrystal, we obtain, by averaging Eq. (30) for all possible values of direction cosines,

$$\bar{K}=-\,(1/10)\,(4k_1+3k_2)\cos^2\theta \ , \tag{32}$$

where θ is the angle between the direction of the measuring magnetic field and that of the annealing field. In the case of an ideal solution ($V=0$), Eqs. (31) reduce to equations derived by Néel[3] and Taniguchi[5].

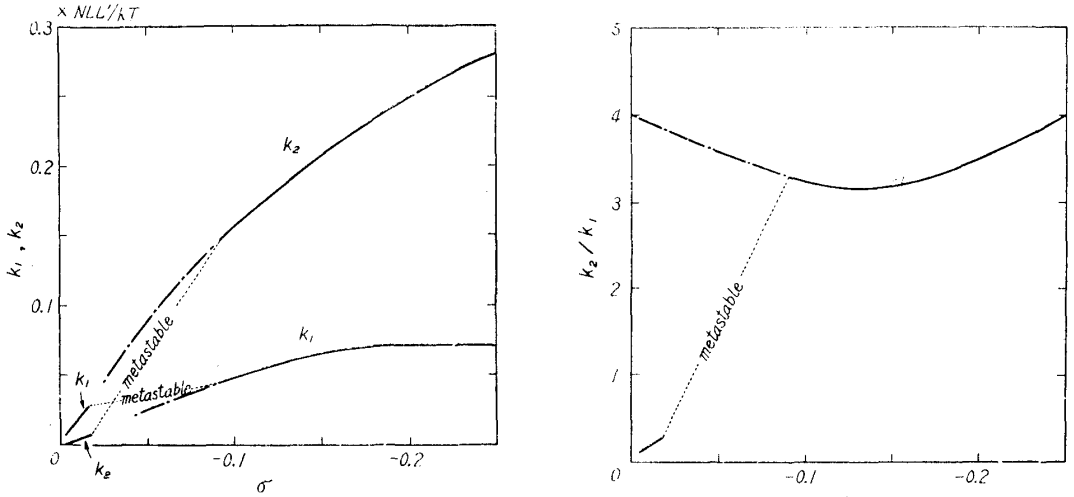
The results of numerical calculations by Eqs. (31) of the dependence of k_1, k_2, and their ratio on the magnetic annealing temperature, T, are given in Fig. 7(a) and (b). As the short-range order develops, k_1, k_2, and k_2/k_1 take values smaller than those for the ideal solution, and they are reduced discontinuously and largely by the development of the long-range order. Configuration-dependent factors in k_1, k_2, and their ratio as functions of the short-range order, $\sigma=-a+$

$c+f$—h, are shown in Fig. 8(a) and (b), which shows that the dependence of k_2 on the ordering is larger than that of k_1. The decrease in k_2/k_1 values with the development of the order is attributed to this dependence.



(a) k_1 and k_2 *vs.* T (b) k_2/k_1 *vs.* T

Fig. 7. Dependence of the equilibrium values of k_1, k_2, and their ratio on the magnetic annealing temperature, T. Chain curves are those for a hypothetical case where the long-range order is absent ($r=1/4$), and dashed curves are those for the ideal solution ($V=0$).



(a) k_1 and k_2 *vs.* σ (b) k_2/k_1 *vs.* σ

Fig. 8. Dependence of the equilibirium values of the configuration-dependent factors in k_1, k_2, and their ratio on the short-range order, σ ($\sigma=-1/4$ and 0 correspond to the perfect disorder and the perfect order, respectively). Chain curves are those for a hypothetical case where the long-range order is absent.

VI. Comparison with experiment and discussion

There is no experiment to be compared with the present calculation which is concerned with the equilibrium properties of the directional oder in the AB_3-type superlattice alloy at various magnetic annealing temperatures.* Chikazumi measured[7] the change in the induced ferromagnetic anisotropy in a Ni_3Fe single

* Quite recently, M. Takahashi and H. Fujimori have studied experimentally the induced anisotropy in Ni_3Fe as dependent on the magnetic annealing temperature and found a dependence very similar to the curves in Fig. 7 (a).

crystal during the magnetic annealing at a nearly fixed temperature. As shown in Fig. 9, experimental values of k_1, k_2, and k_2/k_1 calculated from the data given in his paper vary corresponding to the change in the first magnetocrystalline anisotropy constant, K_1, which indicates the degree of the short-range order. Thus, Fig. 9 may be reasonably compared with Fig. 8. Excepting the initial range of the directional order formation where k_1 and k_2 increase sharply (the right-hand side of Fig. 9), the general feature of the experimental curves is in accordance with the present calculation. There is, however, some discrepancy in the absolute value of k_2/k_1. Theoretically, the value of k_2/k_1 takes 4 at the perfect disorder and decreases from this value as the order develops while the experimental value starts from about 9. A high value of k_2/k_1 in an 83% Ni-Fe single crystal was also reported by Aoyagi[13].

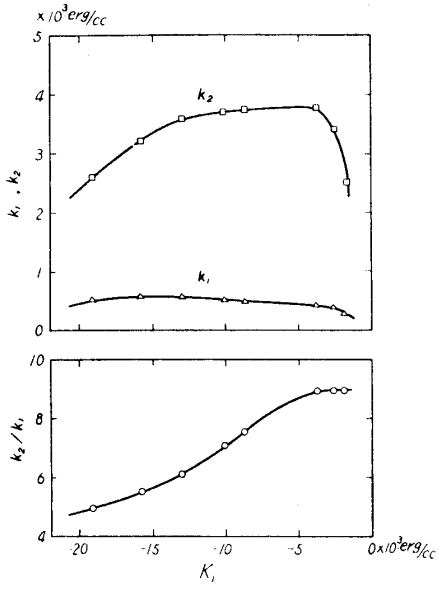


Fig. 9. Experimentally determined k_1, k_2, and k_2/k_1 as a function of the magnetocrystalline anisotropy constant, K_1, in Ni_3Fe annealed magnetically at a nearly fixed temperature (After Chikazumi [7]).

It was suggested[7] that the ratio of about 9 might originate from the nature of the face-centered cubic lattice: Since, in this lattice, some of the nearest neighbors of one atom are also nearest neighbors to each other, some of the B-B atom pairs radiating from the same B atom produce the third B-B pair, thus making a triangular B-B-B arrangement. The deviation of the experimental value of the k_2/k_1 ratio from 4 was attributed to the contribution from these B-B-B arrangements. However, the problem is so complicated to be discussed by the simple theory. In fact, in the present calculation we have counted all kinds of atom pairs as AA, AB, and BB and taken into consideration the above-mentioned nature of the face-centered cubic lattice by adopting the quadruplets approximation, but a k_2/k_1 ratio larger than 4 has not been obtained. Moreover, as the results of the calculation show, the correlation of the directional order with an ordinary superlattice in the equilibrium state can not explain the higher value of the k_2/k_1 ratio. Therefore, it seems that the effect of the relaxation process in the order-disorder transition or of the anti-phase boundary in the superlattice should be further investigated to clarify this problem.

Summary

The directional order induced by magnetic annealing in the face-centered cubic solid solution and its correlation with the order-disorder transition of the AB_3 type were calculated by the quasi-chemical method. The quadruplets approxi-

mation was employed in order to take into consideration the complication involved in the close-packed lattice. Anisotropic long-range order parameters, r_i (i=1, 2, 3), and sixty four parameters representing the numbers of different quadruplets, a_j, b_{ij}, c_{ij}, d_j, e_j, f_{ij}, g_{ij}, and h_j (i=1, 2, 3; j=1, 2, 3, 4), with some geometrical restrictions were introduced to describe both the directional order and the ordinary order, in terms of which the internal energy as the sum of the energies of the neighboring atom pairs, the normalized number of configurations, and hence the free energy of the system could be formulated. A set of simultaneous equations obtained by minimizing the free energy was solved by the method of successive approximation under the assumption that the degree of directional order is not so large. Thus, the equilibrium values of the order parameters were expressed as functions of the annealing temperature and of the values of these parameters in the absence of the magnetic anneal effect. Then, the order parameters as dependent on the annealing temperature in the magnetic field along principal crystallographic directions were computed numerically. The results of calculation indicate that these parameters are affected by ordering and exhibit large discontinuities at the critial temperature, T_c, of the order-disorder transition.

It was found that the factors k_1 and k_2 in the experssion for the ferromagnetic anisotropy associated with directional order varied with the magnetic annealing tempuratere as well as ordering. Numerical calculation showed that the equilibrium values of k_1, k_2, and their ratio k_2/k_1 were smaller than those for the ideal solution and that they exhibited discontinuities at T_c. It was also shown that the dependence of k_2 on the ordering was larger than that of k_1 and that this condition yielded the decrease of k_2/k_1 ratio from the value 4 for the perfect disorder. Thus, the general feature of the induced ferromagnetic anisotropy in the magnetically annealed Ni_3Fe single crystal could be explained by the reuslts of the present calculation.

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